First-principles thermodynamics— specific heat of Mo from density functional theory molecular dynamics simulations

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Multiscale Dynamic Materials Modeling

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Why would we need expensive first principles thermodynamics?

Let us take a look at vacancy diffusion.

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Vacancy mediated diffusion is the main mechanism for mass transport in solids

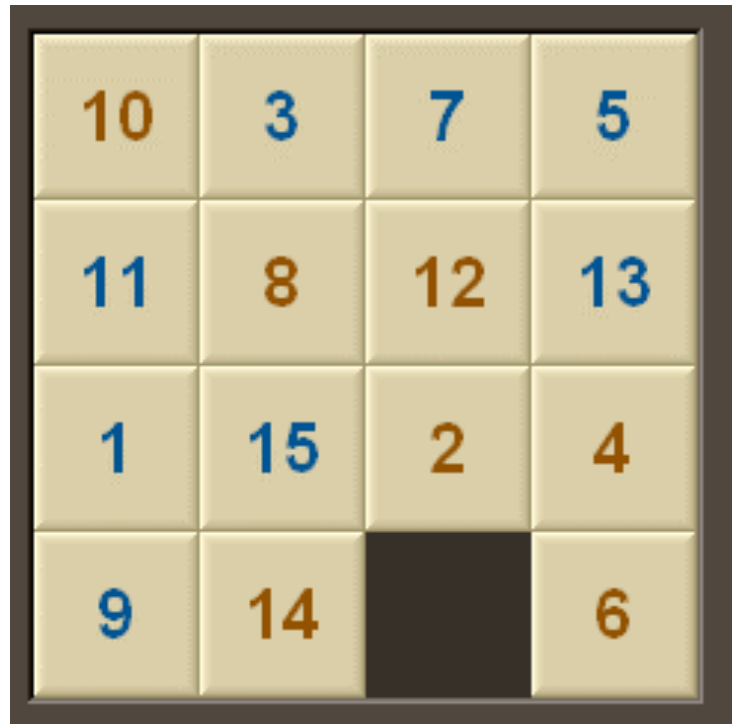| 10	3	7	5
11	8	12	13
1	15	2	4
9	14	16	6

- Vacancies are important for:

  - Self-diffusion

  - Defect migration.

  - Solid phase transformations.

  - Segregation of phase and alloy boundaries.

  - Radiation damage

  - Aging of materials

  - Phase stability

  - Process aware materials modeling

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Vacancy mediated diffusion is the main mechanism for mass transport in solids

| 10	3	7	5
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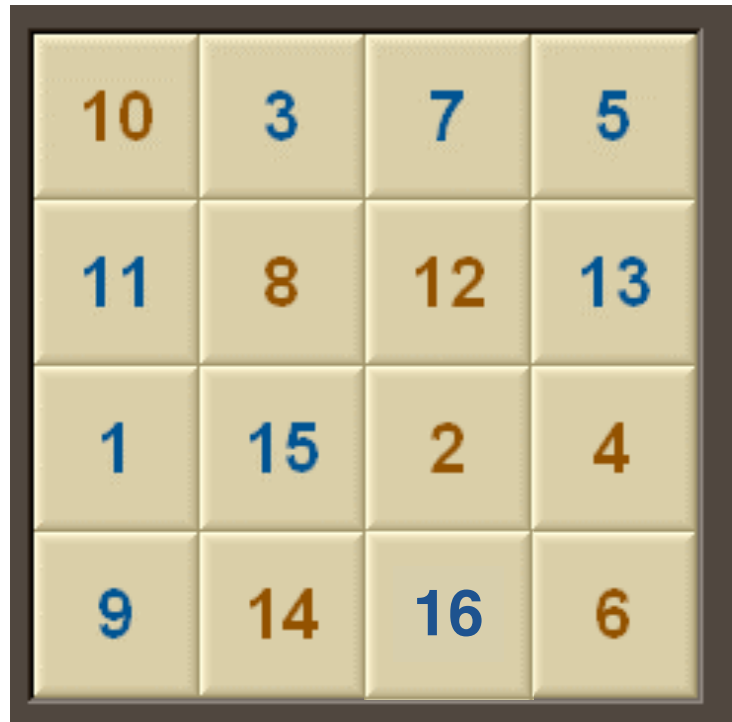
Without the vacancy, there is little hope of moving pieces in the puzzle.

- Vacancies are important for:

  - Self-diffusion

  - Defect migration.

  - Solid phase transformations.

  - Segregation of phase and alloy boundaries.

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Self diffusion in fcc Al: T=0K DFT + EAM anharmonicity at high T, is quantitative

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2002 0K-DFT w surface corrections + Ercolessi-Adams: S_F

2008 0K-DFT w surface corrections + DFT (0K): S_F
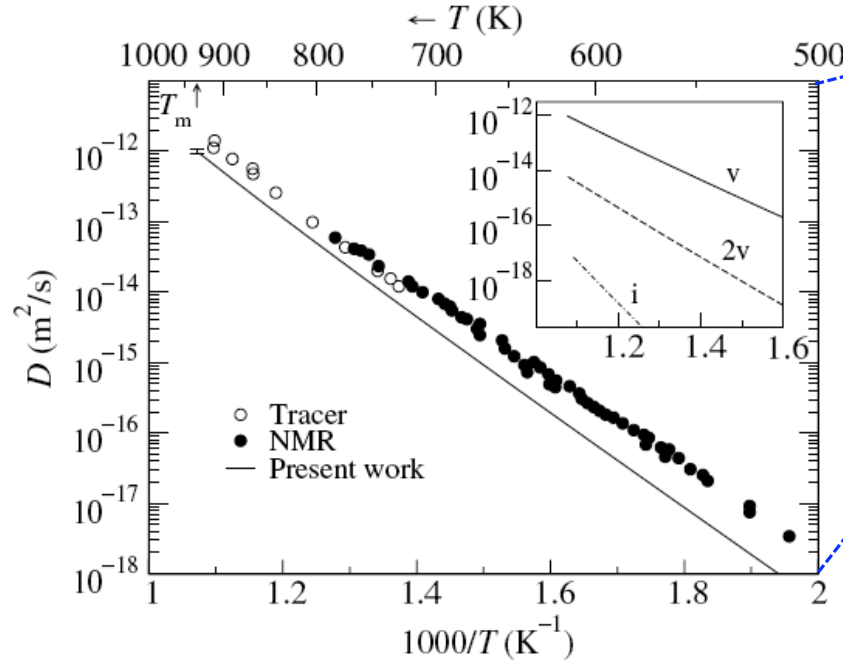
N. Sandberg, B. Magyari-Kope, T.R. Mattsson, PRL **89**, 065901 (2002).
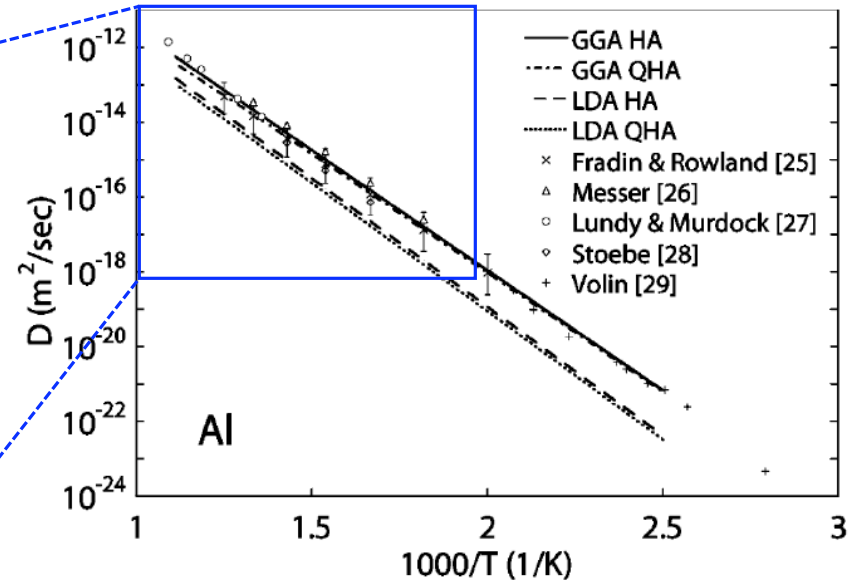
M. Mantina, et al. PRL **100**, 215901 (2008).

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Self diffusion in bcc Mo: T=0K DFT + Finnis-Sinclair model potential: not even close!

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+ anharmonicity from model pot.

+ electronic entropy from ground state

Standard TST
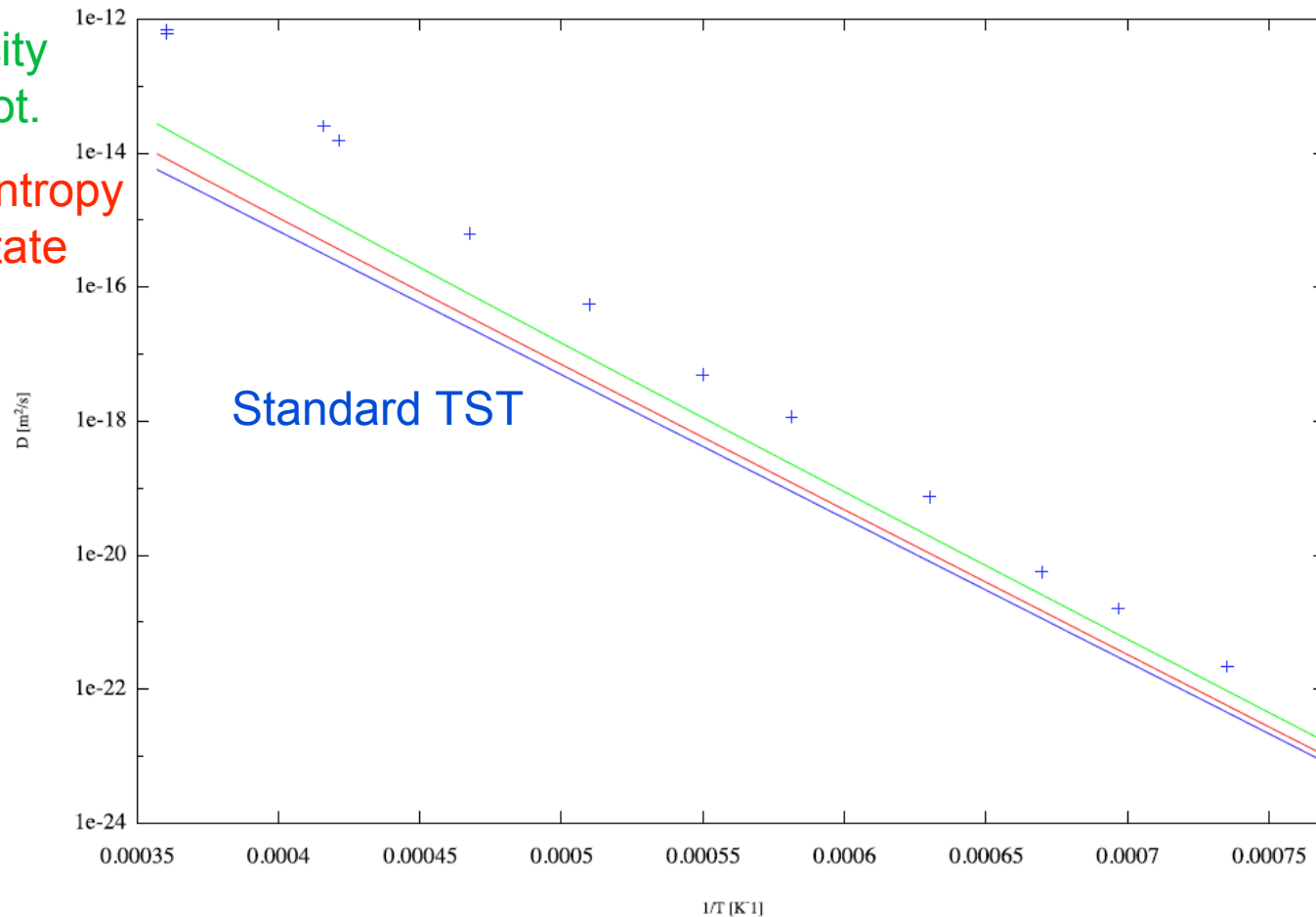
Activation + formation energy
Just fine at low temperature

We need first principles also at high temperature:

Temperature: We need to do first principles molecular dynamics (MD).
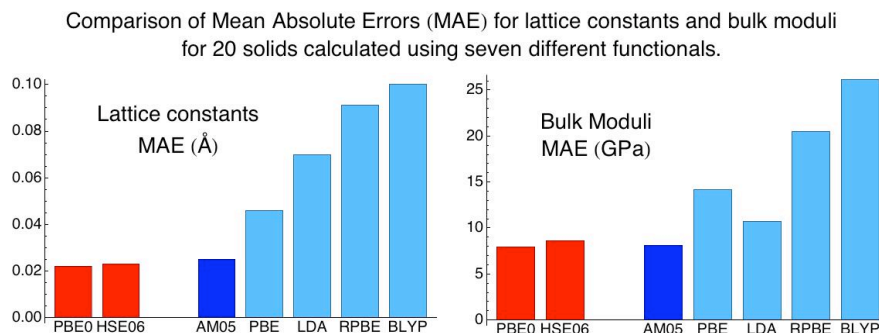
Horribly expensive calculations:
• We need big and fast computers
• Even so, we need as fast a method as possible
• DFT only sensible first principles method
• All electron and hybrids are out of question, they are too slow for MD.
• Pseudo-potentials and sensible and fast exchange-correlation functional needed.
• We have VASP 5 on Red Storm
• VASP 5 includes the AM05 functional (Armiento and Mattsson, PRB **72**, 085108 (2005)).

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What we know about AM05 so far

- AM05 excellent for solids, with a substantial improvement over LDA and PBE. See Haas et al, PRB **79**, 085104 (2009) for the most comprehensive testing to date. AM05 performs as best hybrids for solids:

  Mattsson et al,
  JCP **128**, 084714
  (2008).

Comparison of Mean Absolute Errors (MAE) for lattice constants and bulk moduli for 20 solids calculated using seven different functionals.

Lattice constants MAE (Å)

Bulk Moduli MAE (GPa)

- Contrary to "GGA for solids", AM05 is not specifically designed for solids, but does, for example, molecular reactions almost as well as PBE (MAE 8.08 kcal/mol vs 7.63 kcal/mol on 80+ reactions from the G2 set) (to be published).

- Spin version of AM05 has been available for a while (results in for example Haas et al). Article describing spin-AM05: PRB **79**, 155101 (2009).

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What we know about AM05 so far

- AM05 has no van der Waals, not even faulty. See Haas et al:

Faulty van der Waals in e.g. LDA and PBE, can give highly irrelevant results. AM05 results can be corrected post-processing, and AM05 results can be trusted in compression.

HAAS, TRAN, AND BLAHA
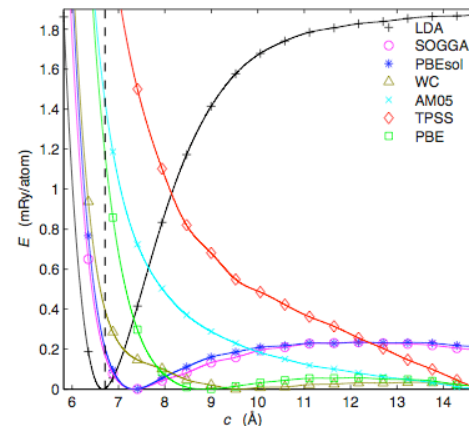
PHYSICAL REVIEW B **79**, 085104 (2009)

FIG. 3. (Color online) Total energy of graphite vs the lattice constant c (the interlayer distance is $c/2$). The in-plane lattice constant a was kept fixed at the experimental value (2.464 Å) for all values of c. The minima for the AM05 and TPSS functionals are either much larger than 15 Å or absent. The vertical dashed line represents the experimental lattice constant ($c_0=6.71$ Å).

TABLE III. Equilibrium lattice constant (in Å, a_0 for Ne and Ar, and c_0 for graphite). The Strukturbericht symbols are indicated in parenthesis.

Method	Graphite (A9)	Ne (A1)	Ar (A1)
LDA	6.7	3.9	4.9
SOGGA	7.3	4.5	5.8
PBEsol	7.3	4.7	5.9
PBE	8.8	4.6	6.0
WC	9.6	4.9	6.4
TPSS	>15	4.9	6.4
AM05	>15	>5.5	>6.7
Expt.	6.71[a]	4.47[b]	5.31[b]

[a]Reference 76.
[b]References 77–79.

- Subroutines for implementation into several types of DFT codes are available at

  http://dft.sandia.gov/functionals/AM05.html
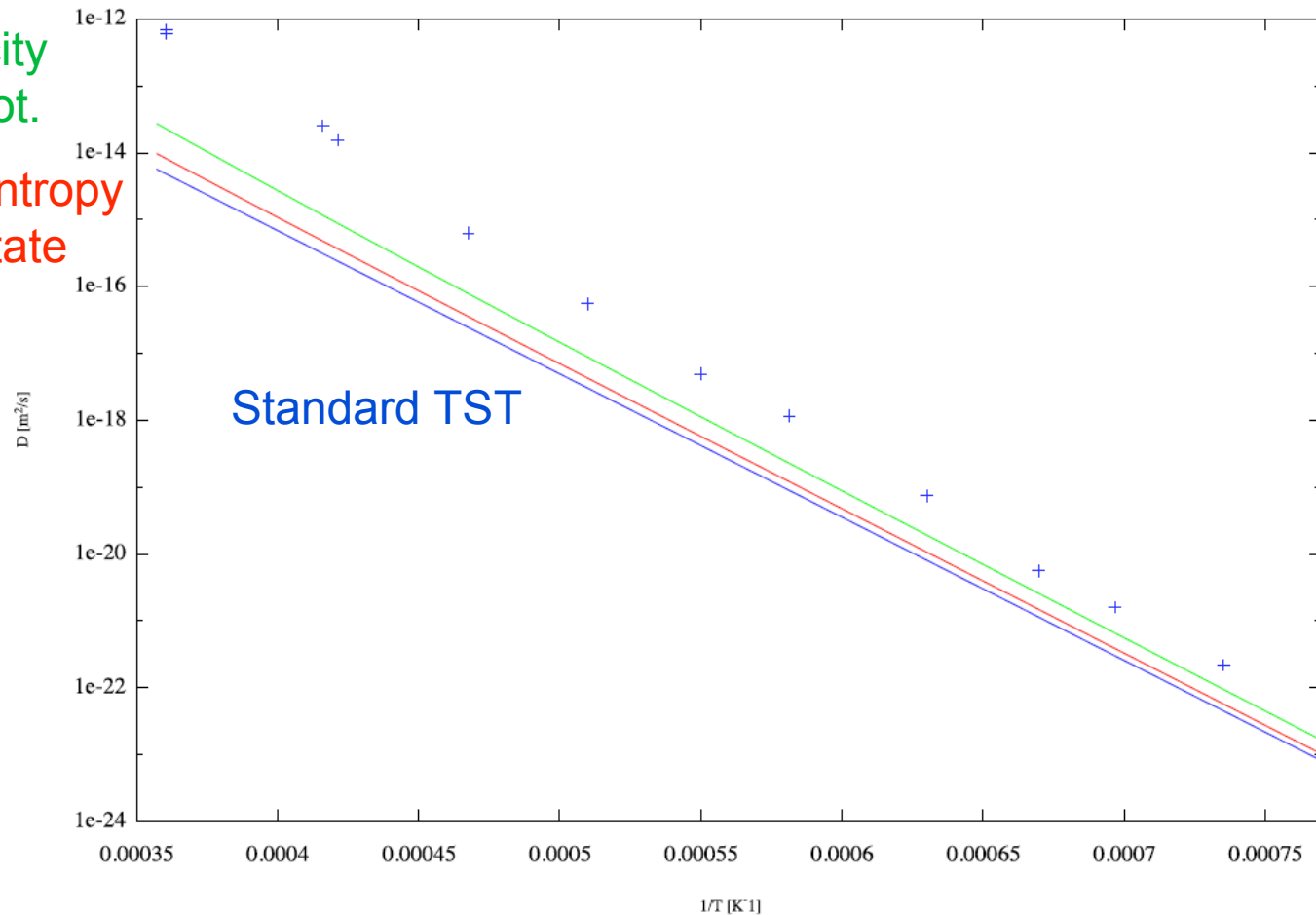
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Self diffusion in bcc Mo: T=0K DFT + Finnis-Sinclair model potential: not even close!

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Self diffusion in bcc molybdenum

Self diffusion coefficient Mo

- Extensive DFT-MD simulations
  - AM05 and PBE XC-functionals.
- 127 Mo atoms for 30 ps
  - Follow the hopping motion of the vacancy, calculate self-diffusion
  - Very demanding simulations, millions of CPU-hours.
- AM05 quantitative results over 11 orders of magnitude.
- AM05 considerably improved accuracy compared to PBE.
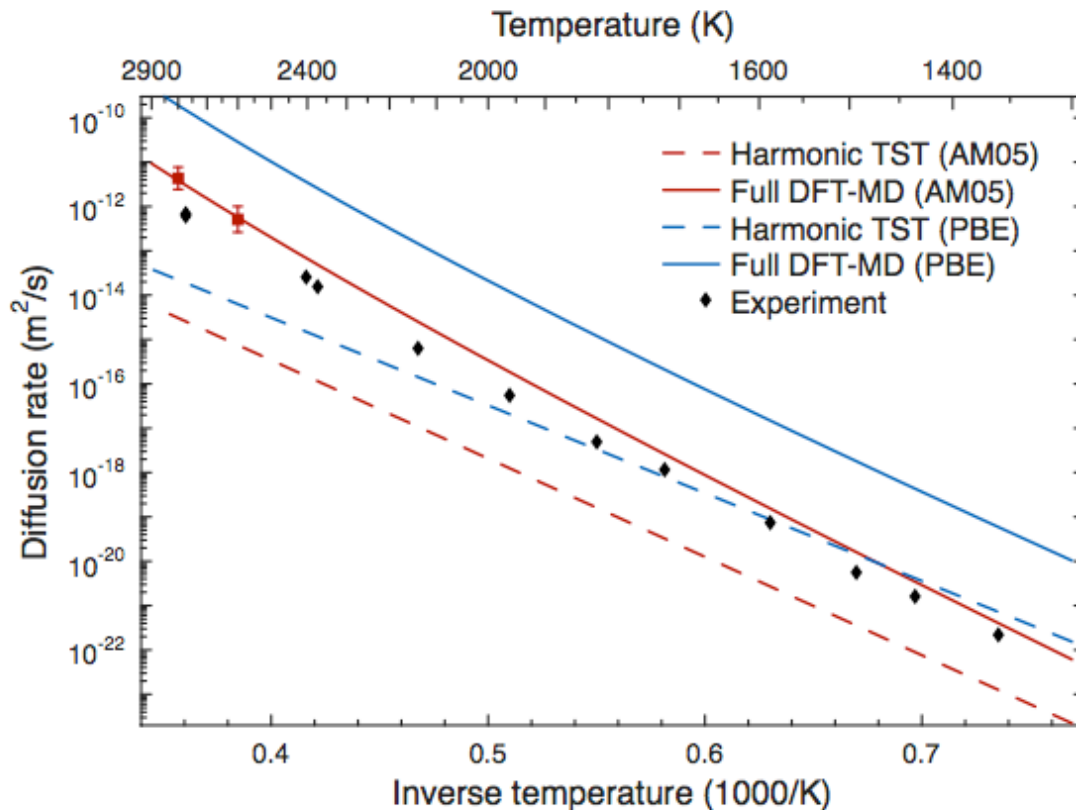
Quantifying the anomalous diffusion of molybdenum by first-principles simulations
TR Mattsson, N. Sandberg, R. Armiento, AE Mattsson

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Now we can start thinking about thermodynamics

Specific heat at constant volume:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

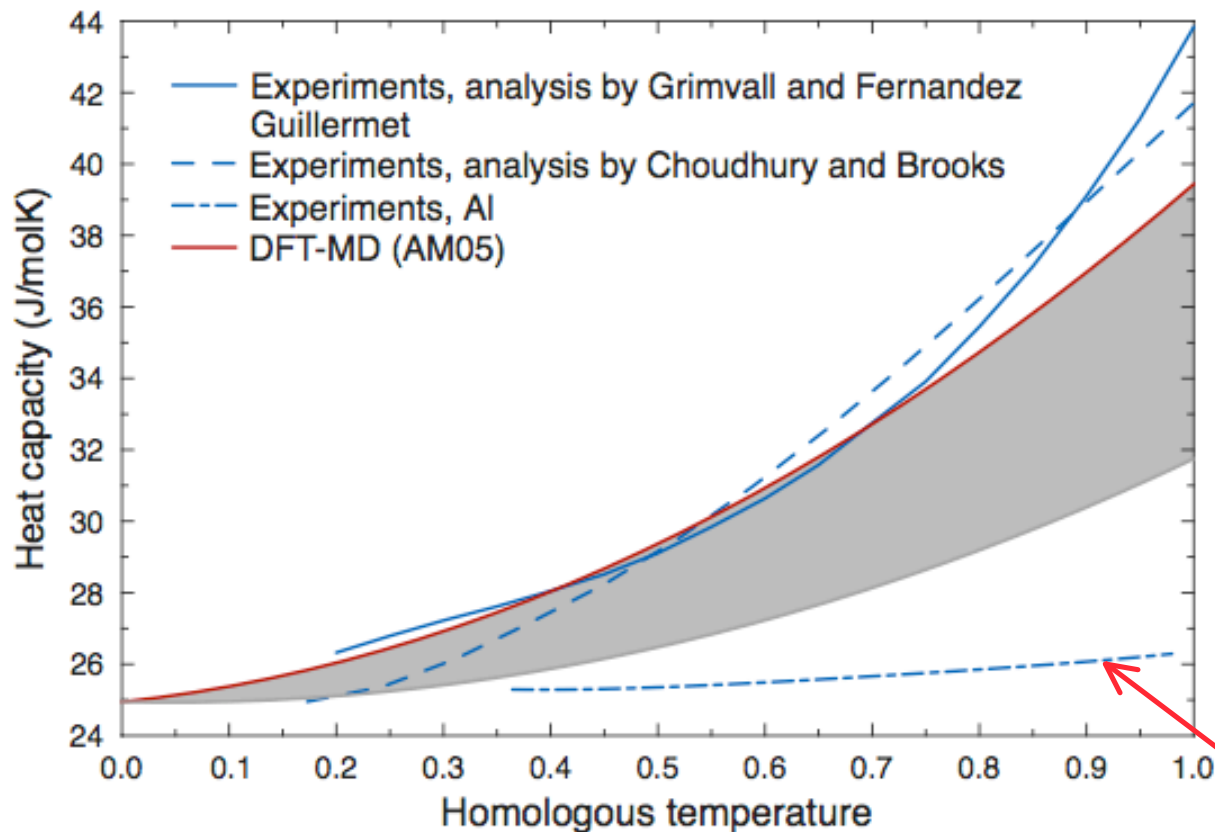Calculate internal energy U at constant volume at different temperatures

Compare to experiment: C_p is measured

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BCC metals display anomalous heat capacity

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Heat capacity (C_V) for Mo

Legend:
- Experiments, analysis by Grimvall and Fernandez Guillermet
- Experiments, analysis by Choudhury and Brooks
- Experiments, Al
- DFT-MD (AM05)

Y-axis: Heat capacity (J/molK)
X-axis: Homologous temperature

- First-principles Density Functional Theory (DFT) simulations
- Finite-temperature DFT crucial
- AM05 XC-functional
- 128-250-432 Mo atoms
- 90% of an-harmonicity captured
- Experimental uncertainties

Al - small, but noticeable An-harmonic contribution

First-principles thermodynamics

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Summary

• For systems and properties where electronic temperature effects are large there is, for the moment, no good alternative to DFT-MD.

• To gain enough confidence in the outcome of these demanding calculations, care is needed in choice of code and in particular exchange-correlation functional.

• However, accurate first principles thermodynamics is possible.

• AM05 is an accurate and fast functional for solids.

• The subsystem functional scheme used to create AM05 promises to be valuable for creating functionals for problematic areas of DFT, such as for Molecular Crystals and Actinides.

• Since AM05 is so different it is a good complement to more standard functionals like LDA and PBE for estimating error bars.

• With improved accuracy of functionals, new standards for acceptable numerical errors will emerge. (You cannot blame the functional any more).

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Thanks!

For your attention.

In collaboration with: Thomas R Mattsson, SNL
Nils Sandberg, Royal Institute of Technology, Sweden,
Rickard Armiento, University of Bayreuth, Germany (now at MIT).

Reprints available at:

www.cs.sandia.gov/~aematts/publicationlist.html
and
dft.sandia.gov/functionals/AM05.html

Questions? Comments?

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